

Core level photoemission study of some superconducting characteristics in the 1-2-3 system

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Abstract : The surface electronic structure as a function of the oxygen content has been studied by means of photoemission of sintered 1-2-3 and BISCCO powders. The influence of oxygen stoichiometry on the core level lineshapes of O, Ba and Cu of YBCO has been reported. Our results indicate that in the YBCO compound, the 531 eV peak of O 1s spectra arises because of an extrinsic contribution only. Oxygen present on the surface and the intergranular space give to rise this peak. The shape of Ba 4d spectra is found to be influenced by ordering of oxygen vacancies in the basal plane. It appears that the low binding energy component (~ 87 eV) of Ba 4d spectra is a measure of the Meissner fraction of the sample. Cu 2p spectra show the presence of Cu 1+ and 2+, and absence of 3+ in the ground state.

Keywords : High temperature superconductivity, X-ray photoemission spectroscopy, oxygen stoichiometry

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1. Introduction

Although, a reasonably consistent picture has emerged about the electronic structure of high temperature superconducting oxides, from the high energy probes such as photoemission and X-ray absorption, some questions are still wide open. For instance, it is interesting to note that, while a widespread consensus exists on the nature and location of oxygen holes [1-5] the nature of core level O 1s photoemission spectrum is still not unambiguously understood. Most of the spectra published so far, show two main structures (at approximately 529 and 531 eV) of variable intensity ratio. Some groups [6, 7] have also reported the growth of a third feature at 533 eV at low temperatures, which they attribute to the formation of O_2^{2-} dimers. There is no controversy about the 529 eV peak and is also observed in CuO, indicating its association with Cu-O bond. But whether the higher binding energy component at ~ 531 eV has a structural origin or it is only due to surface contamination is still an unanswered question. Due to the strong dependence of the intensity of 531 eV peak on the sample surface preparation, many studies have assigned this peak to surface contamination [8-10]. However, some authors have discussed its presence in terms of the intrinsic contribution [11-13]. In polycrystals, cleaved in UHV at room temperature, the 531 eV peak is weak and disappears on mild Ar bombardment. A single

peak with negligible high binding energy component (531 eV) is observed in the O 1s core level spectrum of YBCO single crystal cleaved at 20 K [14]. But 531 eV peak starts developing as soon as the temperature is raised to 50 K. Its growth is attributed to contaminant bulk oxygen that starts diffusing towards the surface at 50 K.

In this paper, we attempt to resolve this controversy on the basis of our detailed study of change in O 1s spectra as a function of oxygen content in the sintered powder of YBCO.

The lineshape of Ba 4d photoemission spectra of YBCO is found to be influenced by the oxygen stoichiometry. Structural studies have revealed that the chemical environment at Ba sites is significantly influenced by the charge distribution and charge transfer among the chains and the conduction Cu-O layers induced by the oxygen stoichiometry [15]. It is found that the Ba 4d spectra is not only related to the oxygen content but also to the degree of ordering of oxygen vacancies.

In the present study, we have attempted to find out the importance of ordering of oxygen vacancies and its effect on Ba 4d core levels. Influence of oxygen content on Cu 2p core levels has also been studied in the sintered powder of YBCO.

2. Experimental

YBCO was prepared by usual solid state reaction, using high purity carbonates and oxides. BISCCO (2223) sample was prepared by mixing Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO in their nominal ratio, and heated at 800°C and 810°C with an intermediate grinding. The sample was then fired at 868°C for more than 72 hrs.

The resistivity measurements were made using Vander Pauw configuration in conventional four probe technique. The average oxygen content was determined by Iodometric Titration method.

XPS measurements were performed in UHV using Mg K X-ray source. Electrons were monitored by a VG CLAM-2 hemispherical analyser. The FWHM was 0.85 eV at 100,000 cps for Mg K radiation on Ag $3d_{5/2}$ peak. To ascertain the surface stability, before each set of measurement sample was scraped repeatedly *in situ* to expose the fresh superconducting grains of correct stoichiometry. Spectra taken after fresh scrapings were found to be reproducible.

3. Results and discussion

O 1s :

To investigate the problem of O 1s photoemission spectrum, a careful study has been made in which oxygen stoichiometry is varied by heating, quenching and sputtering the bulk 1-2-3 sample. The O 1s photoemission spectra are shown in Figure 1 for different status of the sample. Curve 1(a) represents O 1s measurement on the superconducting 1-2-3 sample immediately after insertion into the UHV chamber and shows two peaks at ~532 (which is

dominating) and 529 eV. The sample had a $T_c \sim 92$ K and an oxygen content 6.87. On scraping, the 532 eV peak disappears and the weight of the higher binding energy component (~ 531 eV) decreases (Figure 1(b)). The disappearance of the 532 eV peak on scraping shows that it arises only from an extrinsic contribution. It probably corresponds to contamination of the surface by CO_3 molecules when the starting compounds used in synthesis happen to be carbonates [12]. On subsequent scrapings the weight of 531 eV peak

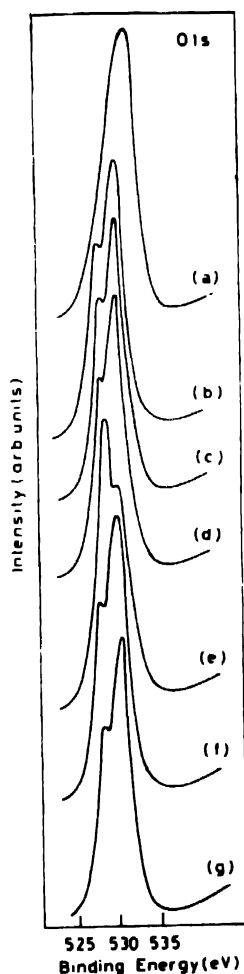


Figure 1. O 1s spectrum of sintered pellet of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: (a) as-grown, (b) scraped in vacuum, (c) heated for 8 hrs at 550°C , (d) quenched to LN_2 temperature from 600°C , (e) Ar ion sputtered for 6 hrs in vacuum, (f) exposed (c) to air, (g) heated for 12 hrs at 550°C in O_2 .

decreases only marginally. This, however, does not mean that the residual intensity of the 531 eV peak derives from the intrinsic oxygen. It has to be remembered that our YBCO sample has got a high density (81.2%) and is very hard to scrape. So, mere scraping is unlikely to remove all the surface and intergranular oxygen present in it. This becomes all the more clear from our measurements on the BISCCO (2223) compound (Figure 2). As

can be seen from it, the 531 eV peak totally disappears on scraping in this case. In comparison to YBCO, BISCCO is more porous (density 55.5%), so mere scraping is adequate to remove all the surface and intergranular oxygen giving rise to a single peak at ~ 529 eV.

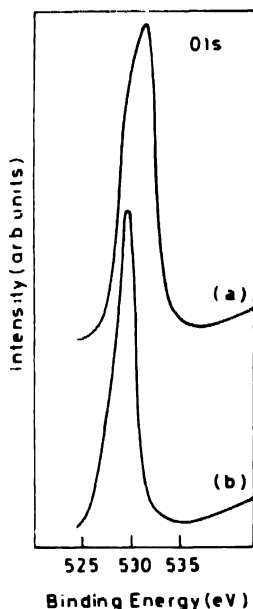


Figure 2. O 1s spectrum of sintered pellet of BISCCO (2223) (a) as-grown, (b) scraped in vacuum

The YBCO sample was then heated to 550°C in air followed by scraping and subsequent measurement (Figure 1(c)). The T_c , on heating went down to 40 K and the oxygen content got depleted to 6.55. The 531 eV peak still continues to dominate despite depletion in intrinsic oxygen content. The sample was then heated and quenched to LNT from 600°C and remeasured after scraping (Figure 1(d)). It had now changed to an insulator and the oxygen content had further gone down to 6.43. The O 1s spectrum however, shows no significant change, with the 531 eV peak still dominating in intensity.

Next, we sputtered the quenched sample *in situ* for 6 hours further reducing the oxygen content from 6.43 to 6.40. There was now a dramatic change in the intensity of the 531 eV peak which reduces drastically (Figure 1(e)). Recapitulating our results therefore, it may be pointed out that although the lattice oxygen content goes down from 6.87 to 6.43 in first heating the sample in air to 550°C and quenching it to LNT from 600°C, the relative intensity of the 531 eV peak stays high and constant. As a matter of fact, the intensity of the 531 eV peak shows no appreciable change from 1(b) to 1(d) even though the intrinsic oxygen content is very different for these samples. The only common factor was that the sample was heated and quenched in air. The obvious conclusion to draw would be that the 531

eV peak owes its origin to the extrinsic oxygen. However, in a recent study done by Balzarotti *et al* [16], the intensity of 531 eV peak was reported to be drastically reduced, when the bulk 1-2-3 sample was heated between 450-550°C *in situ*, and the oxygen content was reduced to ~ 6.3-6.4 from 6.93. There were however, only minor changes observed in O 1s spectra upto 350°C. They have ascribed this reduction in the intensity of 531 eV peak to the removal of intrinsic oxygen from the Cu-O chain sites. If this is true that 531 eV has an intrinsic contribution, our spectra of superconducting and quenched sample should also have shown some decrease in the intensity of the 531 eV peak. But they do not, and the relative ratios of the integrated intensities of 529 and 531 eV peaks were also found to be similar ($I_{529}/I_{531} \sim 0.7$). It is thus very unlikely that the 531 eV could owe its origin to the intrinsic oxygen. Our Ba 4d and Cu 2p core level spectra in which changes are reflected as and when oxygen content is varied, no matter whether the sample is treated *in situ* or in air, further strengthen our argument. Absence of any such change in our O 1s spectra of superconducting and quenched sample implies that the reduction in the intensity of the 531 eV peak, (after heating at 450°C-550 °C) observed by Balzarotti *et al* [16] may have been due to escape of the extrinsic oxygen from the surface and the intergranular space. That is why, when we heated and quenched our sample in air causing depletion in oxygen content (from 6.87 to 6.43), due probably to restoration of surface and intergranular oxygen, no reduction in the intensity of 531 eV peak was observed. On the other hand, on sputtering, even though there was an insignificant reduction in the oxygen content (from 6.43 to 6.40), the intensity of the 531 eV peak was reduced drastically. Adding to these, restoration of the intensity of the 531 eV peak on exposing the sample to air after sputtering (Figure 1(f)) and no further change on reoxygenation (Figure 1(g)), gives us no choice but to conclude that the higher binding energy peak of O 1s core level spectra of YBCO has an extrinsic origin only.

Ba 4d :

Interest in the Ba 4d photoemission spectra derives from the dependence of its lineshape on the oxygen stoichiometry. Ba 4d measurements were therefore also made on YBCO sample and the spectra are shown in Figure 3.

The Ba 4d level for the 92 K superconductor sample consists of two sets of spin orbit split doublets giving rise to characteristic spectra with three peaks (Figure 3(a)). Stenier *et al* [17] and Ford *et al* [11] have ascribed both the high and the low energy components to the superconducting phase. Stoffel *et al* [18] and Liu *et al* [19] have interpreted their data as a surface core level shift but draw opposing conclusions about which peak represents the surface component. Stoffel *et al* [18] have assigned the spin-orbit doublet at higher binding energy to the surface component whereas Liu *et al* [19] have concluded that it is the lower binding energy component that represented the surface component. Recently, Parmigiani *et al* [20] have pointed out that in all Ba core level spectra, the bulk orthorhombic superconducting phase is represented by the lower binding

energy component and the non-superconducting tetragonal phase by the higher binding energy component. This interpretation is, however, doubtful because their spectra in case of sintered bulk and thin film YBCO samples show a higher intensity for the high binding energy component in the superconducting state, i.e. when the orthorhombic phase is dominant. Also, their spectra for a YBCO single crystal, tetragonal phase, show that the lower binding energy component has more intensity than the higher binding energy one.

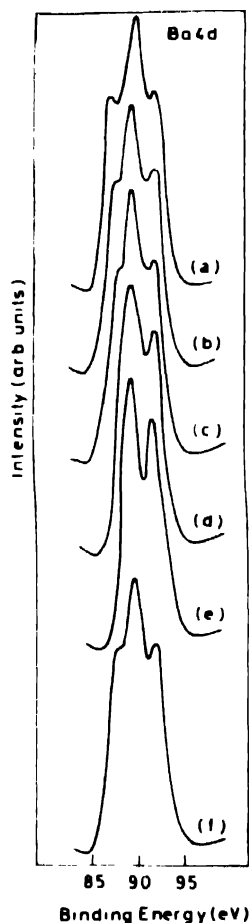


Figure 3. Ba 4d spectrum of sintered pellet of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. (a) as-grown, (b) scraped in vacuum, (c) heated for 8 hrs at 550°C , (d) quenched to LN_2 temperature from 600°C , (e) Ar ion sputtered for 6 hrs in vacuum, (f) heated for 12 hrs at 550°C in O_2 .

These discrepancies in the published data on Ba core levels, showing opposite/different trends for samples subjected to different treatments have further motivated us to make an attempt to explain various features observed in Ba 4d spectrum.

As evident from our measurements, shown in Figure 3, it is only the low binding energy peak in the Ba 4d spectrum that shows a decrease in intensity with scraping and

heating (Figures 3(b) and 3(c)). In case of the quenched (oxygen 6.43) non-superconducting sample (Figure 3(d)), the lower binding energy doublet (~ 87 eV) disappears completely. These results clearly prove : (i) The lower binding energy component does not have a purely extrinsic origin otherwise it should have been present in the quenched sample spectrum too, as quenching has been done in air only. The sample surface is thus identical to those in case of the scraped and the heated sample. (ii) There must be a connection between the low binding energy component and the superconducting properties of the system. The feature reappears when the sputtered sample (Figure 3(e)) is reoxygenated (Figure 3(f)).

It is interesting to note that while in our case the original shape of the Ba $4d$ spectrum and superconductivity is regained on reoxygenation, Balzarotti *et al* [16] have earlier reported that Ba $4d$ spectrum does not regain its original shape on reoxygenation even though the superconductivity gets restored. They have mentioned that the behaviour of two distinct sets of components probably related not only to the oxygen content but also to the degree of ordering of the oxygen vacancies. Although oxygen was reintroduced in their sample also, but because of the short annealing time, oxygen content might have randomly increased in the basal plane but ordering of the vacancies could not be restored. In our case, because of the long annealing time, the ordering of the oxygen vacancies, following their argument, must be also getting restored. Maignan *et al* [21] in their studies on Tl (2201) cuprates, have emphasised the role of two factors, oxygen stoichiometry and its homogeneous distribution in the superconducting behaviour of the sample. The former, they point out, governs the hole carrier density and the latter, the Meissner fraction. They found the Meissner fraction to increase from 6% to 65% when the sample is annealed for a longer period so that a progressive ordering of oxygen vacancies can take place. Applied to the present case it implies that the low energy doublet may emphasise the Meissner fraction rather than just being a signature for superconductivity. May be, because of this reason, Balzarotti *et al* [16], although they do get superconductivity restored in their quickly reoxygenated sample, the low binding energy doublet shows very low intensity, indicating the low superconducting fraction. Measurements on Tl samples are contemplated to further explore, if any of their XPS core level spectra would also show a behaviour on ordering or lack of ordering of oxygen vacancies.

Cu $2p$:

Because of the large hybridization between Cu $3d$ and O $2p$ valence electrons, major changes are expected in the Cu core level with oxygen stoichiometry. The modification of the spectrum can be discussed in terms of relative amounts of Cu^{1+} , Cu^{2+} and Cu^{3+} (Cu $3d^9$ L) configurations in the ground state.

The Cu $2p_{3/2}$ core level spectra of the as grown and scraped surface (Figures 4(a), (b)) indicates the dominance of Cu^{2+} . The signature of divalency is the presence of a satellite at ~ 942 eV which is ascribed to the poorly screened Cu $2p^5 3d^9$ final state. This is

observed in CuO as well. Multiple splitting due to the interaction of the Cu 2*p* core hole with the hole in the 3*d* shell gives rise to the trapezoidal form of the satellite line. The main peak at ~ 933 eV corresponds to a $\text{Cu } 2p^5 3d^{10} \text{O} 2p^5$ state, i.e. a configuration where the Cu core hole is shielded by a charge transfer from an oxygen atom.

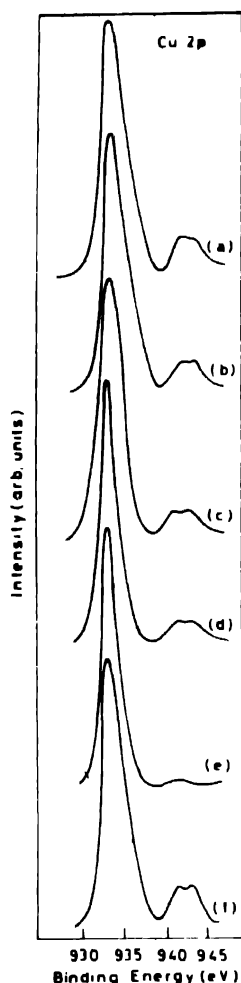


Figure 4. Cu 2*p* spectrum of sintered pellet of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: (a) as-grown, (b) scraped in vacuum, (c) heated for 8 hrs at 550°C, (d) quenched to 1 N₂ temperature from 600°C, (e) Ar ion sputtered for 6 hrs in vacuum, (f) heated for 12 hrs at 550°C in O₂

The main line shows clear asymmetry on the higher binding energy side in the sample having higher oxygen content and the main line tends to increase in breadth with oxygen content (Figures 4(a), (b), (c) and (f)). This weight on the higher binding energy side reduces as oxygen is removed from the sample (see Figure 4(d), (e)). A possible explanation for this has been given by Bianconi *et al* [22] which is based on their Cu 2*p* XPS and Cu L_{2,3} X-ray absorption measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. In that they had identified this contribution as a shakedown of a $3d^9 \underline{\text{L}}$ initial state ($\underline{\text{L}}$ indicates a hole in

the ligand). Thus, there is no clinching evidence for presence of $\text{Cu } 3d^8$, in high energy spectroscopy data, in the ground state.

Reduction in the intensity of the satellite feature on Ar ion sputtering (Figure 4(c)) is because of the conversion of surface Cu^{2+} into Cu^{1+} [12, 23]. Its presence otherwise in the superconducting as well as non-superconducting samples (Figure 4) indicates that it can probably be correlated only to presence of Cu^{2+} and Cu^{3+} ($3d^9$) rather than to presence of superconductivity in the sample.

4. Conclusions

The present photoemission study appears to resolve the controversy regarding the nature of core level O 1s photoemission spectrum of YBCO compound. It is established that the higher binding energy peak (531 eV) arises because of an extrinsic contribution only. This extrinsic contribution arises from the surface and intergranular oxygen in the YBCO sample which is hard to scrape. Disappearance of the high binding energy component on scraping in case of the BISCCO sample, which is easier to scrape, further supports this argument.

It was found that the shape of Ba 4d spectra depends very much on the ordering of oxygen vacancies. It appears that the low binding energy component of Ba 4d spectra is a measure of Meissner fraction of the sample rather than just being a signature of superconductivity.

Cu 2p spectra do not show any feature which can be directly attributed to superconductivity. The spectra however do show the presence of Cu 1+ and 2+, and absence of 3+ (d^8) in the ground state.

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